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Solid-to-Solid Oxidation of a Vanadium(IV) to a Vanadium(V) Compound: Chemisty of a Sulfur-Containing Siderophore

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Ⓢ *Supporting Information*

ABSTRACT: Visible light facilitates a solid-to-solid photochemical aerobic oxidation of a hunter-green microcrystalline oxidovanadium(IV) compound (**1**) to form a black powder of *cis*-dioxidovanadium(V) (**2**) at ambient temperature. The siderophore ligand pyridine-2,6-bis(thiocarboxylic acid), H_2L, is secreted by a microorganism from the *Pseudomonas* genus. This irreversible transformation of a metal monooxo to a metal dioxo complex in the solid state in the absence of solvent is unprecedented. It serves as a proof-of-concept reaction for green chemistry occurring in solid matrixes.

Solid-to-solid transformations have been reported for a range of systems, but the oxidation reactions in solid matrixes have significantly expanded the versatility of these reactions.[1−5] Most of these solid state reactions occurring within organic molecules are reversible in nature and are driven by either light[1,6,7] or heat.[8,9] Solid-state transformations are accompanied by numerous changes in chemical and physical properties such as host−guest behavior,[10−13] modification of the matrix dimensionality,[14−16] magnetic communication,[17,18] and photochemical rearrangements.[7,19−21] In coordination compounds, structural changes are generally more dramatic involving many bond-breaking and -forming processes, so that retention of the product crystallinity becomes a formidable task.[15,19,22,23] Oxidation of a metal oxo species to a metal dioxo in the solid state by gaseous oxygen is an unprecedented process approaching a green reaction requiring no solvent or reagents other than light and air.

Herein we report a photochemical oxidation reaction occurring in the solid state. Specifically, an oxidovanadium(IV) compound, $[V^{IV}O(L)]$ (**1**), containing a sulfur-based siderophore, pyridine-2,6-bis(thiocarboxylic acid) (H_2L), oxidizes via solid-to-solid transformation to form a *cis*-dioxidovanadium(V) complex, $[V^{V}O_2(HL)]$ (**2**), in 100% yield (Figure 1). This reaction is not observed in solution or in the absence of light or oxygen. We have investigated this oxidation reaction by IR, electron paramagnetic resonance (EPR), and multinuclear NMR spectroscopies to document the changes in the metal oxidation state.

The ligand H_2L is a natural product which is produced and released by several strains of the genus *Pseudomonas* when grown in an iron deficient environment.[24] At 198 D, it is the smallest naturally produced extracellular microbial metal chelator, commonly known as a siderophore.[25] While microorganisms commonly produce siderophores, mainly catecholate- and hydroxamate-based, sulfur-containing siderophores are rare.[25] Interest in this natural metabolite increased when it was shown to be involved in the degradation of CCl_4 by *P. stutzeri* and hydrolysis of CCl_4 to CO_2 and HCl by its copper complex.[26,27]

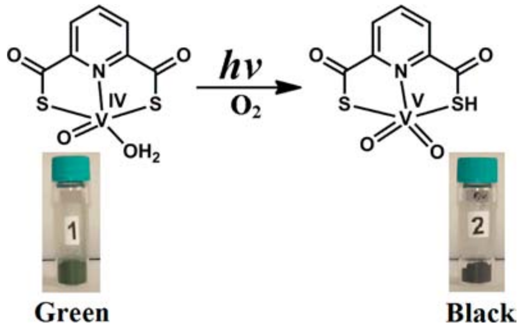

Figure 1. Structures and colors (hunter green and black) of compounds **1** (left) and **2** (right) in the solid state.

The coordination chemistry of H_2L was first reported with iron(2+/3+) showing a tridentate coordination mode with 1:2 metal-to-ligand stoichiometry.[28,29] Subsequent studies with other transition metal ions have shown that mostly divalent and some trivalent metal ions form complexes with H_2L.[24,30−33] The seminal contribution by Krüger and Holm demonstrated that this ligand can stabilize trivalent nickel and can serve as an excellent model for the coordination chemistry that takes place in the [NiFe]hydrogenase enzymes.[33] Few reports on vanadium−sulfur chemistry have explored their novel coordination chemistry;[34−44] however, vanadium complexes with a sulfur-based siderophore, such as H_2L, have not yet been documented.

In the past, H_2L has been synthesized following the procedure of Hildebrand et al.[28,29] The use of toxic and flammable reagents, pyridine and H_2S, has limited access to this ligand.[28] We have synthesized the ligand H_2L using the more convenient approach shown in Scheme 1. Upon treatment of 2,6-pyridinedicarboxylic acid (H_2dipic) with excess thionyl chloride, a light-yellow dicarbonyl dichloride, pdcdc, formed. The pdcdc is then stirred with a saturated aqueous sodium bisulfide until all of the solid pdcdc dissolved. The ligand H_2L is isolated, in 65−70% yield, by adjusting the pH to 1.8.

Compound **1** (Figure 1) is obtained as a hunter-green microcrystalline solid by reacting the ligand H_2L with

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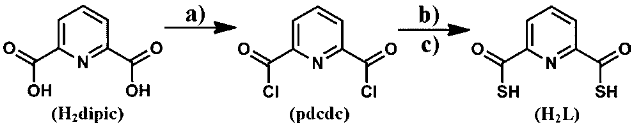
Scheme 1. Synthetic Route to Siderophore H_2L[a]



[a]Conditions: (a) $SOCl_2$, stir; (b) NaHS, H_2O, stir; (c) HCl.

$VO(OR)_3$, where R is either Me, Et, or *i*Pr. Elemental analysis, thermogravimetric analysis (TGA), and electrospray ionization mass spectrometry (ESI-MS) support the composition $[V^{IV}O(L)(H_2O)]$. A strong band at 964 cm^{-1} in the IR spectrum of this compound is assigned to the V═O stretching mode of oxidovanadium(IV).[23] The UV–vis spectrum shows a d–d band as a shoulder at 465 nm. The ESI-MS (positive-ion mode) of compound **1** in CH_3OH shows a peak at m/z 264 ($[\mathbf{1}\text{-}H_2O + H]^+$). TGA of **1** shows a weight loss of 6.3% (calcd 6.4%), which is equivalent to one water per formula unit and thus supports the molecular composition of **1** being $[V^{IV}O(L)(H_2O)]$. The EPR spectrum of compound **1** recorded in a CH_3OH solution at room temperature (Figure S1) displays eight well resolved lines (^{51}V, $I = {}^7/_2$) with $\langle g\rangle = 1.997$ and $\langle A\rangle = 106 \times 10^{-4}$ cm^{-1}, which attests to the existence and stability of the 4+ oxidation state of vanadium.[34,45]

Reacting 2,2′-bipyridyl with compound **1** resulted in a light-brown compound (**3**) in moderate yield (ca. 47%). The IR spectrum of this compound also contains a strong band at 964 cm^{-1} corresponding to the V═O stretching mode of oxidovanadium(IV).[23] The structure of compound **3** was determined by single-crystal X-ray analysis; see Figure 2. The vanadium is in a distorted octahedral geometry in which the three donor atoms (S1, S2, and N3) from the ligand L^{2-} and the N1 atom from the bipyridyl ligand define the basal plane. The V1–O3 [1.605(3) Å][41,42] and average V–S (2.4313 Å) distances are in the expected ranges for oxidovanadium(IV) thio compounds.[41,42] The V1–N2 bond length is large [2.280(4) Å] because of the *trans* effect of the terminal oxo group O3.[43] Because **3** is obtained by derivatization of **1**, we infer that **1** contains oxidovanadium(IV).

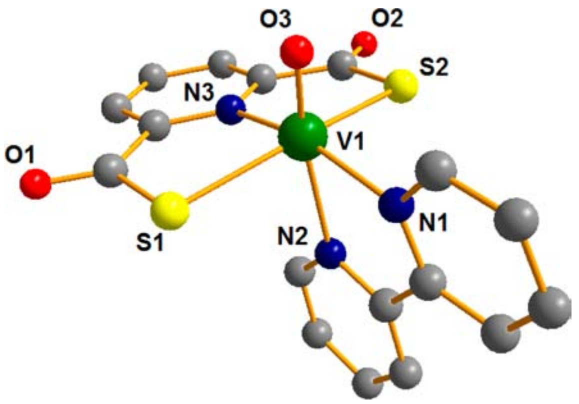


Figure 2. Perspective view and atom-numbering scheme of compound **3**.

Microcrystals of **1**, placed in a petri dish, were allowed to stand in open air at ambient temperature for about 3 months. During this period, the initial hunter-green compound underwent a solid-to-solid oxidation reaction to yield a black product **2**, which is amorphous. The color change during the reaction, shown in Figure 1, is indicative of the molecular change. Both light and oxygen are required for the oxidation reaction to occur, as documented from control experiments carried out in the dark and/or under an argon atmosphere for similar and longer time periods. The black solid no longer exhibits a strong band at 964 cm^{-1} in the IR spectrum; instead, a strong twin-band pattern appears at 990 and 927 cm^{-1}, characteristic of the *cis*-VO_2 moiety.[46] The UV–vis spectrum shows no band corresponding to the d–d transition. These data are consistent with the oxidation of oxidovanadium(IV) to a dioxidovanadium(V) compound in the solid state. Moreover, the appearance of a weak band at 2506 cm^{-1} attests to the presence of an SH group in compound **2**.

To further characterize the oxidation state of vanadium in **2**, ^1H NMR spectroscopy was used. The ^1H NMR spectrum of **2** is shown in Figure 3b and documents that this material no longer contains vanadium(IV). The pyridine ring protons appear at 8.31 and 8.63 ppm, with the couplings, integration, and chemical shifts of a metal complex of H_2L (Figure 3b). The singlet at 7.90 ppm in Figure 3b is assigned to the SH proton from the thiocarboxylic acid group. Coordination of the SH group to the vanadium(V) center shifts this singlet SH proton downfield from the free ligand H_2L signal at 5.72 ppm (Figure 3a). The ^{51}V NMR spectrum (Figure 3c) shows only one signal at −548 ppm and confirms the presence of vanadium(V) in compound **2**.

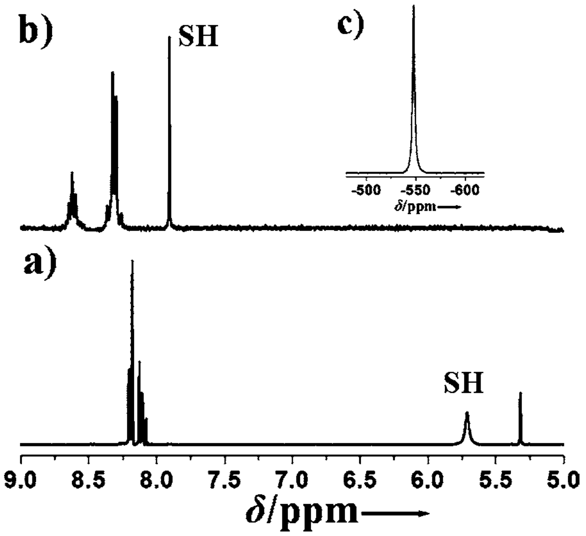


Figure 3. ^1H NMR spectra of the ligand H_2L (bottom, a) and compound **2** (top, b) acquired in CD_2Cl_2 and CD_3OD, respectively. The inset c shows the ^{51}V NMR spectrum of **2** in CD_3OD. Spectra were recorded at 25 °C.

Compound **1** is the first metal complex that undergoes solid-to-solid oxidation in the presence of light and is also unique with regard to its coordination chemistry exhibited in the solid state. In complex **2**, the coordination number remains the same; however, the oxidation of vanadium results in conversion of an aqua group to an oxo group. Two systems have been reported to undergo solid-to-solid oxidations.[2,4,5] However, in these systems, oxidation takes place after the crystal was ground to a powder and suspended in a solvent such as DMSO or H_2O containing an oxidant such as I_2 or O_2.[2,4,5] These reactions provided the impetus for the development of a solid-to-solid oxidation reaction that takes place even in the absence of solvent. Green and sustainable chemistry has become important because of the increasing pressures to reduce waste and side products in chemical processing.[47,48] The oxidation reaction presented here, albeit very slow, demonstrates a solid-to-solid conversion without the need for the addition of solvent or reagents other than oxygen.

In summary, we have observed an oxidation reaction taking place in the solid state. The solid-to-solid irreversible transformation of an oxidovanadium(IV) to a *cis*-dioxidovanadium(V) compound is readily observed by the color change. This solid-state oxidation is triggered by visible light in the presence of oxygen and oxidizes the discrete vanadium(IV) complex by a one-electron-transfer reaction to a vanadium(V) species. This conversion of a metal oxo compound to a metal dioxo complex is the first report in metal–oxygen chemistry occurring in a solid matrix and documents the feasibility of green processes taking place in the absence of solvent.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and characterization details, tables of relevant crystallographic data, tables of important metrical parameters, X-ray crystallographic files in CIF format for compound **3**, and the EPR spectrum of compound **1** in CH_3OH. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 867913 contains the supplementary crystallographic data for this paper (compound **3**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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